

A STUDY OF THE PHASE RELATIONS OF
ZIRCONIA-TITANIA AND
ZIRCONIA-TITANIA-SILICA

BY

HAROLD GENE SOWMAN

B.S., University of Illinois, 1948

M.S., University of Illinois, 1949

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CERAMIC ENGINEERING
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1951

URBANA, ILLINOIS

1951

A STUDY OF THE PHASE RELATIONS OF
ZIRCONIA-TITANIA AND
ZIRCONIA-TITANIA-SILICA

BY

HAROLD GENE SOWMAN

B.S., University of Illinois, 1948

M.S., University of Illinois, 1949

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CERAMIC ENGINEERING
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1951

URBANA, ILLINOIS

1951

ACKNOWLEDGMENT

The author wishes to express his appreciation to the Titanium Alloy Division of the National Lead Company whose fellowship grant made this work possible, to Dr. A. I. Andrews, head of the Department of Ceramic Engineering, who supervised this study, and to G. F. Stockdale, E. D. Lynch, A. L. Friedberg, and A. W. Allen of the Department of Ceramic Engineering for material aid and discussions during the course of this investigation.



A STUDY OF THE PHASE RELATIONS OF ZIRCONIA-TITANIA AND ZIRCONIA-TITANIA-SILICA

INTRODUCTION

The purpose of this study was to obtain sufficient data to make it possible to diagram the phase relations of the binary system, $\text{ZrO}_2\text{-TiO}_2$ and the ternary system, $\text{ZrO}_2\text{-TiO}_2\text{-SiO}_2$.

A literature survey revealed that no previous work was published on the phase relations of the ternary system, $\text{ZrO}_2\text{-TiO}_2\text{-SiO}_2$. The binary system, $\text{ZrO}_2\text{-TiO}_2$ was investigated to a very limited extent by Bussem¹.

EXPERIMENTAL PROCEDURE

Two methods of study were used in this investigation. The first of these methods was the quenching technique, which consisted principally of heating the materials to the desired temperature, soaking, quenching in water or mercury, and analyzing by X-ray diffraction equipment*. The second method used was the high-temperature X-ray diffraction technique. Briefly, this involved the X-raying of specimens while actually being heated at the desired temperature.

Special furnaces were designed for high-temperature X-ray diffraction. The first of these was capable of reaching a specimen temperature of 1500°C . This furnace was quite similar to one previously designed by Valkenburg and McMurdie². The second of these furnaces was capable of attaining a specimen temperature of 1750°C . It involved the use of two Pt.-20% Rh. resistor strips. One of these strips acted as both heating element and sample holder. The other acted only as a heating element.

*North American Philips X-ray Spectrometer

Materials used in this work were of very high purity. Samples were prepared carefully to insure homogeneous specimens. The process consisted of drying, weighing, wet mixing, grinding, sintering and grinding again. Two more sintering and grinding operations followed. Many samples were prepared without the sintering operation. In some cases, the formation of intermediate compounds or solid solutions at the sintering temperature of 1400°C hindered the attainment of equilibrium conditions. Many hours of heating were required to reach equilibrium when it was necessary to decompose the previously formed solid solutions or compounds.

DISCUSSION OF RESULTS

Preliminary investigations of the binary system $\text{ZrO}_2\text{-TiO}_2$ showed that the quenching technique was not satisfactory in studying compositions of higher than 65% ZrO_2 (by weight) in this system. The quenching process failed to freeze the higher temperature forms of ZrO_2 believed to be present. In the range of 65-85% ZrO_2 , both the monoclinic and tetragonal forms of ZrO_2 appeared. With more than 85% ZrO_2 , only the monoclinic form appeared. It was believed that only the tetragonal form of ZrO_2 should have been present. Later studies by the high-temperature X-ray diffraction technique supported this thought. This technique was used in studying both the binary system $\text{ZrO}_2\text{-TiO}_2$ and the ternary system $\text{ZrO}_2\text{-TiO}_2\text{-SiO}_2$.

From this investigation, the system $\text{ZrO}_2\text{-TiO}_2$ was found to have no intermediate compounds. Solid solution areas existed on both sides of the diagram. An eutectic point was found to exist at a composition of 50-55% ZrO_2 (by weight) and a temperature of $1600^{\circ} \pm 20^{\circ}\text{C}$. At the eutectic temperature, TiO_2 (rutile) took 21% ZrO_2 into its crystal structure. At the same temperature, the maximum solubility of TiO_2 in ZrO_2 (tetragonal) was 37%.

The ternary system $\text{ZrO}_2\text{-TiO}_2\text{-SiO}_2$ contained no ternary compounds. An eutectic point was found at 2% ZrO_2 , 10%

TiO₂, and 88% SiO₂ at approximately 1500°C. The system contained the phase areas of TiO₂ (rutile), ZrO₂ (tetragonal), and SiO₂ (cristobalite). The areas of cubic ZrO₂ and zircon (ZrSiO₄) were believed to exist. However, because the investigation of this system was limited, the presence of these areas was not verified. Similarly, the extent of solid solution in the system was not studied.

BIBLIOGRAPHY

1. W. Bussem, C. Schusterius, and A. Ungewiss, "X-ray Investigation of Binary Systems TiO₂-MgO, ZrO₂-MgO, and ZrO₂-TiO₂," *Ber. Deut. Keram. Ges.*, 18 (10) 433-43 (1937).
2. A. V. Valkenburg, Jr., and H. F. McMurdie, "High-Temperature X-ray Diffraction Apparatus," *Bull. Am. Ceram. Soc.*, 26 (5) 139-42 (1947).

VITA

Harold Gene Sowman was born on July 21, 1923 in Murphysboro, Illinois. He attended elementary schools in Murphysboro and East St. Louis, Illinois. After graduating from East St. Louis high school in 1941, he entered the University of Illinois. His college career was interrupted when he entered the Army of the United States in January, 1943. After his release from active duty, and appointment to the Organized Reserve Corps in July, 1946, he returned to the University of Illinois. He received the degree of Bachelor of Science in Ceramic Engineering in 1948. An industrial fellowship granted by the Titanium Alloy Division of The National Lead Company allowed him to study in the graduate college at the University of Illinois. He received the degree of Master of Science in Ceramic Engineering in 1949. A continuation of the Titanium Alloy fellowship allowed him to study towards the degree of Doctor of Philosophy.

He is a member of the American Ceramic Society, Sigma Xi, and Keramos.

Publication:

"A Quenching Furnace for High-Temperature Studies of Small Specimens", J. Am. Ceram. Soc., 33 (12) 365-6 (1950) (with A. I. Andrews).



Digitized by the Internet Archive
in 2026

